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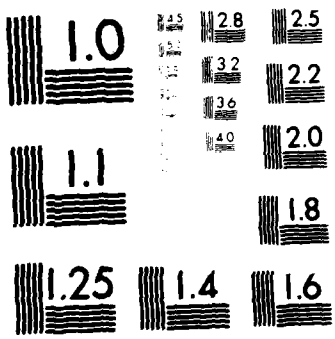

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Principal progress was achieved in the field classical studies of diatom dissociation. 3-D trajectory calculations of dissociating bromine and fluorine were conducted over a range of temperatures, and using several significantly different potential energy surfaces.

A library consisting over a two million trajectories was accummulated. These trajectories were used to test the strong collision assumption, important in several theories of unimolecular reactions and in some theories of thermal diatom dissociation. The assumption was shown to be not valid for the case of dissociating bromine and fluorine. Properties of the steady state of dissociating diatoms were investigated. Papers, now in preparation, involve study of nonequilibrium energy and angular momentum distribution functions; accumulation, interpretation and classification of data on inelastic and reactive collisions; and study of scaling factors and vibrational-rotational ../2

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coupling in dissociating diatoms.

Experiments, still in progress, aimed at measuring recombination rates of fluorine atoms. Time delayed photoelectric effect was explained in terms of a release of trapped electrons at the surface of photocathode.

FINAL SCIENTIFIC REPORT

AFOSR 84-0127

STUDY IN MOLECULAR LASERS

by

Professor George Burns

Department of Chemistry

University of Toronto

Inclusive Dates: June 1, 1984 - May 31, 1985

One of the important types of reactions occuring in molecular lasers is the diatom dissociation-atomic recombination reaction. Over the past fifty years, a number of theoretical models for these reactions in inert gases were proposed. The different theories stressed the importance of different physical phenomena which influence the reaction in a specific way. Today, too many, rather than too few, theories fit the data, which normally are experimental rate constants and their temperature dependencies. However, neither one single theory, nor a judical combination of them can be considered as the most reasonable. This is because it has not been possible to experimentally test various dynamical or statistical assumptions used in these theories.

The classical 3-D trajectory technique provides an alternative method for testing mechanistic processes which are responsible for dissociation-recombination. A study of classical trajectory data deemed quite appropriate because most of today's understanding of chemical reactions is still based on classical mechanics.

One of the limitations of the 3-D trajectory technique was its relatively high cost in computer dollars. Not only calculations of individual trajectories were time-consuming, but the storage of massive amount of data was impractically large. Therefore, usually a relatively small number of trajectories, aimed at the computation of a well defined reaction observable such as the rate constant was secured in each study. However, to assess various statistical and dynamical factors affecting dissociation-recombination with a reasonable degree of precision, much larger trajectory ensembles had to be generated.

Rapid improvements in computer technology made it possible to develop reasonably efficient computer programmes for such calculations. Ensembles, consisting of hundreds of thousands trajectories, can now be generated on computers, at a cost which is small compared to the overall cost of the project.

The AFOSR Grant 84-0127 made it possible to assemble a library consisting of two million 3-D trajectories. These trajectories include, primarily, dissociation of fluorine and bromine in an argon bath at a range of realistic temperatures and for a set of experimentally acceptable, as well as mechanistically intriguing potential energy surfaces (PES).

While trajectories were assembled, the properties of large trajectory ensembles were also investigated. In one such study, relative nonequilibrium energy distribution (RNED) functions were studied using an ensemble of 44,400 trajectories. Deviations from equilibrium were found to be significant, but the strong collisions, involving a large amount of diatom-to-atom energy transfer, were rare and affected RNED only over a limited energy range. It was concluded that the strong collision assumption, widely employed in theories of unimolecular reactions and important in some theories of diatom dissociation, is not applicable to the latter type of reactions. These findings provide an additional support to a set of weak-collision theories of diatomic dissociation. In another study, five trajectory ensembles, totalling over 100,000 trajectories were used to investigate the properties of the steady state of dissociating diatoms in a linear regime, i.e. with recombination neglected. It was found that the steady state was precisely determinable and unique. Therefore, the same steady state was obtained even if the initial distribution functions, from which it was generated, were very different.

It was demonstrated in many earlier investigations that the nature of the PES determines rate constants for many types of reactions. Therefore, it was common to assume that PES can significantly affect diatom dissociation rate constants as well. For this reason, in many 3-D trajectory studies of diatom dissociation, the most precise PES were used; much excellent work was performed to calculate accurately quantum mechanical PES, especially for hydrogen-inert gas systems. However, the importance of PES in the case of

dissociation-recombination was never adequately tested.

Consequently, a part of the trajectory library was used to study the importance of PES. Fluorine dissociation, which was not studied previously by trajectory method, was selected for this work. Although the fluorine dissociation energy for all three surfaces was the same, the difference between these surfaces was as large as can be allowed by the uncertainty in available spectroscopic data. Furthermore, the PES were constructed in such a way as to test the effect of various parameters which, it was suggested in the past, may affect the mechanism of the dissociation reaction. It was found that an increase in diatom anharmonicity tends to increase the equiquilibrium reaction cross-section, but this phenomenon is largely compensated by nonequilibrium effects, which are responsible for depopulation of the most energetic and reactive states. Consequently, although mechanisms of dissociation were indeed affected by PES, rate constants for the three sufraces used were the same within 15 percent.

The papers, now in preparation, use the entire trajectory library to (1) obtain reactive and inelastic collision cross sections and scaling laws for diatomic molecules, (2) calculate relative nonequilibrium energy, and angular momentum (squared) distribution functions, (3) study vibrational-rotation coupling effects and (4) compute total and microcanonical rate constants, and their temperature dependence. The ensembles employed are sufficiently large to insure that the results obtained are sufficiently accurate to ascribe the remaining difference, between the 3-D trajectory data and corresponding experimental findings, to quantum mechanical effects. These papers will be published primarily in the J. Phys. Chem. and J. Chem. Phys.

Experiments, still in progress, aimed at measuring recombination rates of fluorine atoms. Time delayed photoelectric effect in photosensitive semiconductors was explained in terms of a release of trapped electrons at their surfaces.

Dr. L. K. Cohen, a postdoctoral fellow is associated with this work. He received his Ph.D. in elementary particle physics from Cornell.

PUBLICATIONS:

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"Study in Molecular Lasers," G. Burns, Final Scientific Report, 1985.

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